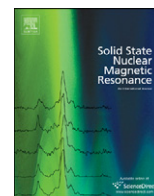




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Solid-state nuclear magnetic resonance investigations of the nature, property, and activity of acid sites on solid catalysts

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ABSTRACT

Further progress in the field of heterogeneous catalysis depends on our knowledge of the nature and behavior of surface sites on solid catalysts and of the mechanisms of chemical reactions catalyzed by these materials. In the past decades, solid-state NMR spectroscopy has been developed to an important tool for routine characterization of solid catalysts. The present work gives a review on experimental approaches and applications of solid-state NMR spectroscopy for investigating Brønsted and Lewis sites on solid acids. Studies focusing on the generation of surface sites via post-synthesis modification routes of microporous and mesoporous materials support the development of new and the improvement of existing catalyst systems. High-temperature and flow techniques of in situ solid-state NMR spectroscopy allow a deeper insight into the mechanisms of heterogeneously catalyzed reactions and open the way for studying the activity of acidic surface sites. They help to clarify the activation of reactants on Brønsted and Lewis acid sites and improve our understanding of mechanisms affecting the selectivity of acid-catalyzed reactions.

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Abbreviations: ²⁷Al, aluminum nuclei; Beta, zeolite with structure type BEA; deH,Na-Y, dealuminated zeolite Y; MAS, magic-angle spinning; MCM-22, zeolite with structure type MWW; MIL-53, metal-organic framework with aluminum as cation; NMR, nuclear magnetic resonance; RUB-18, zeolite with structure type RWR; Y, zeolite with faujasite structure; ZSM-5, zeolite with structure type MFI; *A_i*, integral intensity of an NMR signal; *c_i*, concentration of nuclei “*i*” in a sample under study; *C_{QC}*, quadrupole coupling constant; *d_{OH-O}*, oxygen–oxygen distance; *eQ*, electric quadrupole moment; *I*, nuclear spin; MCM-41, material with mesoporous pore structure; *m_i*, mass of the sample under study containing the nuclei “*i*”; MOF, metal-organic framework; MOR, zeolite with mordenite structure; PA, proton affinity; PPh₃, triphenylphosphine; PyrH⁺, pyridinium ion; Q₈M₈, octakis(trimethylsiloxy)-silsesquioxane; *S_i*, electronegativity of atom *i*; *S^m*, mean Sanderson electronegativity; SBA-15, material with mesoporous pore structure; TMP, trimethylphosphine; TMPO, trimethylphosphine oxide; USY, ultra-stabilized zeolite Y; UV/vis, ultraviolet and visible spectral range; $\Delta\delta_{1H}$, adsorbate-induced low-field resonance shift; $\Delta\nu_{1/2}^{MAS}$, residual line width of a MAS NMR signal; η_Q , asymmetry parameter of the electric field gradient; $\tilde{\nu}_{OH}$, wavenumber hydroxyl stretching vibration; ν_{rot} , sample spinning frequency; Θ , angle between the axis of the sample spinning and the direction of the external magnetic field; Θ_m , magic angle; τ_c , correlation time of thermal motions; τ_{rot} , period of the MAS spinning

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1. Introduction

The development of efficient, safe, and environmentally friendly chemical technologies is an important requirement of the modern chemical industry. Solid acids are doing this work and are able to replace liquid acids and catalysts with low efficiency [1–3]. Hydrocarbons play a key role as fuels, energy sources, as well as reactants and final products in most of the chemical processes [4,5]. Due to the impending depletion of fossil-based resources, more efficient and cleaner chemical processes must be developed. Even now, hydrocarbons can be produced not only from coal, crude oil, and natural gas, but also from renewable biomass [6]. Motivated by this, chemists and engineers seek to utilize solid acids in hydrocarbon reactions with high conversion and selectivity to the desired products. For the tailoring of solid acids, it is essential to study the formation and properties of their surface sites, i.e., of Brønsted and Lewis acid sites. In most applications, heterogeneously catalyzed reactions are initiated or promoted by solid acids via the activation and protonation of the reactants [7]. In this connection, questions regarding the nature of Brønsted and Lewis acid sites, their number, strength, and location as well as cooperative effects must be clarified. Brønsted and Lewis acid sites show different performances at the initial stages of heterogeneously catalyzed reactions. Therefore, also the understanding of their chemical function helps in designing novel solid catalysts for heterogeneously catalyzed reactions, which are more efficient, safer, and environmentally benign.

Since more than three decades, solid-state NMR spectroscopy is demonstrating a high potential for the study of the local structure of framework atoms in solid catalysts [8–10]. The present work focuses on experimental approaches and applications of solid-state NMR spectroscopy for investigating Brønsted and Lewis acid sites on activated solid catalysts. Despite most of the solid-state NMR techniques suitable for characterizing solid acids can be applied with commercially available equipment, the number of research groups utilizing these methods is still small. Therefore, the first part of this work focuses on general strategies for characterizing the properties of acid sites on solids by solid-state NMR spectroscopy. The second part gives an overview on studies of the formation of Brønsted and Lewis acid sites by modifying the catalyst framework or preparation of extra-framework species. The third part focuses on investigations of the reactivity of acidic surface site in heterogeneously catalyzed reactions, e.g., by application of H/D exchange experiments and *in situ* solid-state NMR techniques.

Zeolites stand in the center of the reviewed works, not only because these microporous materials are very important catalysts in the chemical industry, but also due to their specific advantages as well-defined model systems. But also other solid adsorbates and catalyst systems, such as flame-derived silica–alumina, mesoporous materials, heteropoly acids, and metal–organic frameworks, are considered for demonstrating the general importance of the described solid-state NMR approaches.

2. Solid-state NMR characterization of surface sites on solid catalysts

2.1. Experimental approaches of solid-state NMR spectroscopy on activated solid catalysts

Solid-state NMR spectroscopy allows the determination of the type, strength, accessibility, and concentration of surface sites [11–16]. Via one- and two-dimensional solid-state NMR techniques, parameters of the local structure of the catalyst framework and their surface sites are available [8–10,17–24]. Hydroxyl protons acting as catalytically active Brønsted acid sites can be investigated in a direct manner by ^1H MAS NMR spectroscopy [12–15]. The resolution of ^1H MAS NMR spectra recorded by modern solid-state NMR spectrometers is suitable for distinguishing the different types of hydroxyl groups via their chemical shifts, $\delta_{1\text{H}}$. As in the case of Lewis acid sites, however, the strength and accessibility of these sites are preferentially studied upon adsorption of probe molecules. As a result of their interactions with surface sites, the ^1H , ^2H , ^{13}C , ^{15}N , and ^{31}P nuclei of the hydroxyl groups and probe molecules change their NMR spectroscopic parameters in a characteristic manner. An important advantage of NMR spectroscopy is that spectra can be measured quantitatively, which means that a direct dependence of their signal intensities on the spin numbers can be obtained. This property is utilized to determine the concentration of surface sites and adsorbate molecules using an internal or external intensity standard.

In the past decades, the limitations in the spectral resolution of solid-state NMR spectra were overcome by rapid sample spinning around an axis in the magic angle of $\Theta = 54.7^\circ$ to the direction of the external magnetic field (MAS) [25,26]. Using turbines with a gas bearing, sample spinning frequencies, ν_{rot} , of up to 67 kHz are reached for a rotor with the inner diameter of 0.9 mm [27]. Generally, narrowing by MAS requires low thermal mobility of the nuclei under study. Narrowing by MAS is reached, if the correlation time of thermal mobility, τ_c , is large in comparison with the period of the sample spinning ($\tau_c \gg \tau_{\text{rot}} = 1/\nu_{\text{rot}}$) [28]. In the case of low thermal motion, the residual line width $\Delta\nu_{1/2}^{\text{MAS}}$ of MAS NMR central lines of solids is affected by homonuclear magnetic dipole–dipole interactions, which can be reduced either by further increasing the sample spinning frequency, ν_{rot} , or by the application of a multiple-pulse sequence [29,30]. The resolution of MAS NMR spectra may be affected by inhomogeneities of the external magnetic field, misadjustment of the magic angle, thermal motions and exchange processes [26], heteronuclear magnetic dipole–dipole interaction with quadrupole nuclei [31], anisotropy of the magnetic susceptibility [32], and, last but not least, a distribution of the isotropic chemical shift. If the signals are influenced by inhomogeneous line broadening effects, the resolution can be improved by increasing the flux density, B_0 , of the external magnetic field. In the case of spin $I > 1/2$ nuclei, which are involved in quadrupolar interactions due to their

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